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FINAL REPORT

on

PARAMETER-FREE ELECTRONIC CALCULATIONS
IN CRYSTALS AND THIN FILMS

to

DEPARTMENT OF THE AIR FORCE
ELECTRONIC AND SOLID STATE SCIENCES

February 24, 1978

by

R. E. Euwema and I. Shavitt

Contract No. F-44620-76-C-0026

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Three major sets of computer programs have been extensively modified and extended. These programs are a molecular code for finite clusters of atoms with the coding optimized for clusters with cubic point group symmetry, a thin film code for several interacting infinite two-dimensional sheets of atoms, and a crystal code for an infinite number of atoms with cubic symmetry. These programs provide a predictive capability for clusters and platelets of atoms, surfaces and perfect crystals through first-principles calculations at the

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Unrestricted Hartree-Fock level. These programs have been provided to
and used by several USAF personnel.

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ABSTRACT

In order to carry out the physics outlined in the contract proposal, three major sets of computer programs have been extensively modified and extended. They calculate various electronic properties of systems of atoms in the Unrestricted Hartree-Fock (UHF) approximation. The programs are: (1) a molecular code for finite clusters of atoms, with the coding optimized for clusters with cubic point group symmetry; (2) a thin film code for several interacting infinite two-dimensional sheets of atoms; and (3) a crystal code for an infinite number of atoms with cubic symmetry. These three sets of programs provide a predictive capability for clusters and platelets of atoms, surfaces and perfect crystals through first-principles calculations at the UHF level. The molecular programs allow studies of imperfect surfaces and crystals in which impurity atoms, dislocations, vacancies, surface reconstructions, etc., are involved.

The molecular code is operational and has been used by us to study carbon clusters containing five and seventeen atoms and fifteen-atom lithium clusters. Scientists at AFAL/DHR have used this code to study the electronic properties of the nitrogen impurity in diamond. For the carbon five-atom cluster, it was found that the electronic density matrix near the central atom is close to that for an infinite crystal. The calculated atom-spacing of the seventeen-atom cluster is within one-percent of the experimental value for diamond. This code has also been used in preliminary studies of the electronic properties of small carbon platelets.

The current thin film code uses s and p Cartesian Gaussian basis functions and is designed for the symmetry of the (111) face of diamond. The UHF code for the perfect crystal also uses s and p Cartesian Gaussian basis functions.

SUMMARY OF RESULTS

I.   Significance of the Research

Three distinct sets of Unrestricted Hartree-Fock (UHF) programs have been developed. The molecular code (appropriate for small clusters and platelets) is fully operational (with an spd basis). The thin film surface code is operational (with an sp basis) for the (111) face of diamond. The crystal program (with sp basis) has been written but not fully debugged. The thin film programs are the only ones in existence that have been developed to the UHF level of accuracy. The cluster programs incorporate the fastest integral packages in existence, use powerful integral approximations, and have been carefully optimized for the cubic point group symmetry.

A large amount of physics of direct interest to the Air Force can be done with these programs, provided adequate computer access is available. The strong similarities between the different program sets (UHF, Cartesian Gaussian basis sets, integral approximations) will allow valuable comparisons of the electronic properties of clusters, surfaces and perfect crystals. These properties include one-electron energy levels and their associated band widths and band gaps, and the atom-projected density matrix (whose diagonal elements give the charge density in the vicinity of any chosen atom). The comparison of bulk energy bands with thin film energy bands is particularly important for understanding the fundamental physics of various electronic devices. Cluster and platelet calculations (which handle cases where one does not have perfect two or three-dimensional periodicity) are very important in materials science. Examples are ion migration through crystals, electron energies near impurities or dislocations, surface reconstruction, and reactions

at surfaces. Comparisons of cluster calculations with bulk or film calcu-
lations can test whether the clusters are sufficiently large to model real-
istically the physical phenomena of interest. Thus, development of these
three program sets is a necessary first step to performing a large number
of accurate calculations directly related to practical problems in device
physics, materials, etc.

II. Molecular Code

The contract proposal states that a fast molecular code using
Cartesian Gaussians would be employed. The two-electron integral package
would be extracted from the molecular code and inserted into the surface and
bulk programs. At present, the fastest integral package for s and p Cartesian
Gaussian basis functions is contained in GAUSSIAN-70 (G-70), written at the
Carnegie Institute of Technology by Professor Pople and his students. We
consequently chose G70 to form the nucleus for the present AFOSR contract
work.

It was decided to modify G70 before extracting the relevant pieces
for use in the other codes. There were several reasons for this decision.

(1) It was felt that a significant amount of work relevant to the
contract could be done with the molecular code in cases where perfect two
or three dimensional translational symmetry was violated. Examples are ion
migration in solids, impurity atom physics in crystals, reactions at surfaces
and atom reconstruction at surfaces.

(2) It was necessary to obtain considerable familiarity with the intricacies of the code in order to be able to export sections to other programs.

(3) Most of the programming algorithms developed for the molecular code could be easily taken over later to the thin film and crystal codes.

Consequently, the following major changes were made to G70. (We label the resulting code GH76.)

(1) Very flexible data handling and program handling procedures, developed at ARL, were installed to facilitate program development.

(2) A symmetry analysis of the molecular system reduces the number of two-electron integrals which must be evaluated and handled. Any subgroup of the 48 element cubic point group is acceptable.

(3) Two integral approximations developed by us at ARL were installed. One involves the pseudocharge of a basis function pair, while the other involves the product of two pseudocharges. The first integral approximation has proved extremely useful in cluster calculations, while the second has saved so little time that it has been taken out of GH76. It is still extremely powerful for the surface and crystal programs however.

(4) Routines which handle d basis functions were installed twice. Dr. P. C. Hariharan had written relevant G70 routines at Carnegie Mellon University for the IBM 360. We modified these routines for inclusion into GH76. Later, we heard that a new, extremely powerful algorithm had been developed for two-electron integrals involving d basis functions by Professor H. F. King and coworkers at the State University of New York at Buffalo.

Their routines are incorporated into a molecular code called HONDO. We used the appropriate routines from HONDO (with their permission) in our program package (the H in GH76), speeding up the integration time for d basis functions by roughly a factor of two.

(5) Programs to calculate X-ray structure factors and directional Compton profiles were added to GH76. Because we needed to study the electronic density matrix in the vicinity of individual atoms (surface atoms or bulk atoms), we incorporated the basic idea behind the Mulliken population analysis to project out the structure factors, directional Compton profiles and total energy for each atom of the cluster.

(6) Programs were written to simulate a cluster of atoms in an external environment, i.e., to simulate the rest of the crystal surrounding an impurity and its immediate neighbors. The hope was to calculate accurately the properties of a small cluster of atoms, but in an environment which simulates the other atoms in a crystal or surface. We were unsuccessful in our preliminary attempts, and temporarily abandoned the study in order to proceed with the development of the thin film and crystal codes. However, we feel that the idea is sound and merits more work. An alternative approach in which many of the electrons on peripheral atoms are treated with pseudopotentials, while a more complete treatment is used for the atoms in the interior of the cluster, has been examined, and shows considerable promise.

(7) Pseudopotential methods were incorporated into our programs so that the atomic core electrons would not have to be explicitly included in the calculation. Calculations are very much faster when only the valence electrons need be considered. Dr. Luis Kahn of Battelle is a leading authority on this procedure. He was kind enough to donate his programs, which were then appropriately modified for inclusion in GH76.

(8) Contour plotting and three-dimensional perspective programs were obtained and built into GH76 so that wavefunctions and charge densities of clusters can be graphically displayed. This facility allows a visual comparison of densities obtained from cluster, surface and bulk calculations. It is also a useful method for visually displaying the details of the electron bonding at surfaces and in crystals.

(9) Extensive modifications were made to the portions of the programs that self-consistently determine the UHF wavefunctions. The code was streamlined and dynamic dimensioning was introduced so that large clusters could be more easily run. A considerably more efficient algorithm was implemented to process the two-electron integrals.

The following physics were done with GH76.

(1) Calculations were performed on a five-atom carbon cluster, the atoms being arranged in a diamond crystal structure. It was found that in the case where all 12 dangling bond electrons have the same spin, all of the cluster results (band gap, valence band width, X-ray structure factors, directional Compton profiles and the binding energy) were close to the crystalline results. Our Mulliken projection procedure was necessary in this investigation to project out the density matrix for the central atom of the cluster. Further details are given in Appendix A.

(2) The total energy of a 17-atom carbon cluster was calculated with a minimal basis set for several atom spacings. The equilibrium atom spacing was within one-percent of the diamond crystal spacing. The properties of the central atom of the cluster were again most nearly crystalline for the case where all 36 dangling bond electrons have the same spin.

(3) Fifteen-atom lithium crystals were calculated in collaboration with Dr. Luis Kahn. The directional Compton profiles for the central atom were close to the crystalline values. Further details are given in Appendix C.

(4) A study was made in collaboration with Dr. Luis Kahn to determine the best way to obtain the all-electron density matrix from the pseudopotential valence-orbital calculation. Complications arise because the orbitals obtained from the pseudopotential calculation are not orthogonal to the atomic core orbitals, and do not have the correct number of nodes. We developed and tested a procedure which gives a density matrix within one-percent of that obtained from a comparable (but much more time-consuming) all-electron calculation. This knowledge is very important for our surface and crystalline studies for which the pseudopotential procedure should be used for all of the calculations involving atoms heavier than neon. Further details are given in Appendix B.

(5) A study was made comparing all-electron and several types of pseudopotential calculations on a cluster of five carbon atoms in a diamond crystal structure. The study included the use of pseudopotentials for the core electrons of the peripheral four atoms while treating the central atom fully (with all electrons included specifically). Also, the pseudopotential calculations were carried out both with normal (all electron) basis sets and with valence basis sets developed specifically for pseudopotential calculations. Further details are given in Appendix D.

The first three results indicate that many crystalline properties can be successfully obtained from small cluster calculations with GH76 if

the Mulliken projection procedure is used to obtain the properties of the central atom. The fourth result shows that the density matrix and associated properties as well as the energetics can be obtained to useful precision with the pseudopotential procedure. The fifth result demonstrates one practical procedure for including peripheral atoms at lower levels of approximation than for interior atoms in cluster calculations.

The GH76 programs have been distributed in various states of completeness to several other groups. Dr. Ronald Greene of AFAL/DHR used them to study the nitrogen impurity in diamond. Dr. J. Ivey of Mound Lab (ERDA) used this program to study the properties of hydrogen dissolved in metals. Dr. P. Deutch of the Army Ballistic Research Lab has used pieces of GH76, as has Dr. R. Jaffe of NASA Ames Research Center. Dr. T. C. Collins of AFOSR has used GH76 to calculate the properties of Polymers. Dr. R. J. Bartlett of Battelle has used these codes for a study of the electronic structure of catalytic nickel surfaces. The program has also been provided to Dr. M. W. Ribarsky of the Georgia Institute of Technology and to Dr. D. W. Jennison of Sandia Laboratories.

III. Thin Film and Crystal Codes

It became a major programming effort to incorporate the GH76 s-p integral package into the surface and bulk programs. Previously, both codes handled each two-electron integral over four basis functions separately. GH76 gains its speed and efficiency from doing blocks of integrals simutaneously. P-orbitals have the same Gaussian exponents as s orbitals, and all of the s-x-y-z blocks of integrals for all four functions are calculated at once.

The incorporation of this powerful, time-saving feature involved substantial changes in the logical structure of the programs. Consequently, what initially appeared at contract-proposal time to require some weeks of work turned out to require many man-months of work. Long delays and limitations on access to the Wright-Patterson Air Force Base computer hampered this work considerably and limited its scope.

The thin film programs were converted first. They were debugged as much as possible on the Battelle computers at Battelle expense. The programs were then run on the WPAFB computers with a realistic Gaussian basis. Early results appeared very reasonable for a two-atom layer film of diamond, but extensive production computations were impossible due to very limited computer access and very slow service at WPAFB.

The crystal programs have also been restructured and rewritten to handle integrals in blocks. They have first been debugged for small calculations on the Battelle computer at Battelle expense (with a trial basis), but final debugging with a more realistic basis at WPAFB could not be completed due to computer access limitations.

Changes to the surface and crystal programs included the following:

(1) The GH76 one- and two-electron integral packages for s-p functions were installed, with the appropriate logical restructuring.

(2) The ARL Gaussian lobe-oriented integral approximation was scrapped and replaced by an approximation based upon a moment expansion of the charge distribution of the basis function product.

(3) The Ewald procedure (which finds the potential of the infinitely repeating array of charge distributions) was revised to use this same moment expansion.

Extensions to include d basis functions were contemplated, but implementation could not be carried out due to time limitations and computer access limitations.

PERSONNEL

Funded by AFOSR.

R. N. Euwema

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PUBLICATIONS

1. S. Goldstein, L. A. Curtiss, and R. N. Euwema, "UHF Calculations for Five-Atom Diamond Clusters", J. Physics $\underline{C}$, $\underline{9}$, 4131 (1976). Attached as Appendix A.

2. R. N. Euwema and L. R. Kahn, "The Accuracy of First-Order Density Matrices Obtained by Electronic Structure Methods Involving the Valence Electrons Only", J. Chem. Phys. $\underline{66}$, 306 (1977). Attached as Appendix B.

COUPLING ACTIVITIES

J. Ivey   Monsanto Research Corp. (ERDA)
                                 Mound Laboratories
                                 Centerville, Ohio

P. Deutsch   Army Ballistic Research Laboratory
                                 Aberdeen Proving Ground
                                 Maryland

R. Greene   AFAL/DHR
C. Aldrich   WPAFB, Ohio

T. C. Collins   AFOSR
                                 Washington, D. C.

R. Jaffe   NASA
                                 Ames Research Center
                                 Moffitt Field, California

R. Bartlett   Battelle Columbus Labs

L. B. Kahn   Battelle Columbus (funded by NASA)

M. W. Ribarsky   Georgia Institute of Technology

D. W. Jennison   Sandia Laboratories

APPENDIX A

UHF CALCULATIONS FOR FIVE-ATOM DIAMOND CLUSTERS

UHF calculations for five-atom diamond clusters

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Abstract. X-ray structure factors and directional Compton profiles are calculated for diamond (cubic carbon) using a self-consistent field unrestricted Hartree–Fock procedure on a cluster of five carbon atoms. A Mulliken population analysis procedure is used to isolate results to be associated with the central atom. The choice of a high spin state for the cluster yields reasonable agreement with the experimental and theoretical results for crystalline diamond.

1. Introduction

The Hartree–Fock (HF) equations have been solved previously for diamond, and selected crystalline properties have been compared with experiment. The calculated x-ray structure factors (Euwema *et al* 1973) and directional Compton profiles (Wepfer *et al* 1974) which measure the electronic charge and momentum distributions respectively, are in satisfactory agreement with experimental results (Clark 1964, quoting Gotlicher and Wolfel 1959; Reed and Eisenberger 1972). The one-electron energies and the cohesive energy are what one would expect when correlation has been completely neglected. However, the crystalline HF formalism has the disadvantages of requiring much computer time and effort, and of requiring complete translational symmetry. This formalism and the present crystalline HF computer programs cannot be readily extended to treat more complex crystals, impurities, or surfaces.

The purpose of this paper is to demonstrate the feasibility of obtaining certain crystalline results from unrestricted HF (UHF) (Pople and Nesbet 1954) calculations on very small clusters. In particular, we shall display x-ray structure factors and directional Compton profiles for the central atom of a five-atom diamond cluster as well as the average over the cluster. Results for the central atom agree reasonably well with those of the infinite crystal. In order to obtain this agreement, it was necessary to choose the correct spin multiplicity for the cluster, and to employ the Mulliken population analysis procedure to divide the density matrix into portions associated with each of the individual atoms. The spin multiplicity results have important implications for surface calculations on covalently bonded materials.

In §2, we discuss the computational details, including the Mulliken prescription used to divide up the density matrix. The question of spin multiplicity is treated in §3, while §4 and §5 are devoted to discussions of the structure factors and Compton profiles. The results are then summarized in §6.

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2. Computational method

The self-consistent-field UHF procedure has been used to calculate one-electron energies, total energies, and one-electron orbitals, $\Psi_\mu(r)$, for a five-atom carbon cluster, employing a modified version of the Gaussian 70 program package of Pople *et al.*[†] We used the 11s/5p cartesian gaussian carbon basis of Pople and Binkley (1975), contracted to 4s/3p. The carbon atoms have the coordinates $(0, 0, 0)$, $a/4(1, 1, 1)$, $a/4(1, -1, -1)$, $a/4(-1, -1, 1)$ and $a/4(-1, 1, -1)$. The diamond lattice constant, a, is 3·56 Å. The atoms form a tetrahedron, and the distance between the centre atom and any one of those at the corners is the nearest-neighbour distance in diamond.

The first-order density matrix is obtained by summing over the filled UHF orbitals:

$$\rho(r, r') = \sum_{\substack{\text{filled} \\ \text{states}}} \Psi_\mu(r)\Psi_\mu^\dagger(r'). \tag{1}$$

The Mulliken population analysis procedure (Mulliken 1955) is then used to assign parts of ρ to the individual atoms in the cluster as follows. The orbitals are expanded in the contracted gaussian basis functions, $\phi_a(r - R_a)$, associated with the atoms, $\{a\}$, at positions $\{R_a\}$. Expanding the density matrix in terms of the basis functions, one obtains

$$\rho(r, r') = \sum_{ab} \sum_{\alpha\beta} A_{\alpha\beta}^{ab} \phi_\alpha(r - R_a) \phi_\beta(r' - R_a) \tag{2a}$$

$$= \sum_{ab} \rho_{ab}(r, r') \tag{2b}$$

where ρ_{ab} is that part of the density matrix associated with the pair of atoms a and b. Following the Mulliken prescription, we assign half of each term, ρ_{ab}, to atomic site a and half to site b:

$$\rho(r, r') = \sum_c \left[\rho_{cc}(r, r') + \frac{1}{2} \sum_{d \neq c} (\rho_{cd}(r, r') + \rho_{dc}(r, r')) \right] \tag{3a}$$

$$= \sum_c \rho_c(r, r'). \tag{3b}$$

This decomposition of ρ can then be used to calculate the structure factors and Compton profiles for the individual atoms of the cluster.

The Mulliken decomposition is basis dependent for small molecules. An extreme example would involve using a rich basis on the central atom of the five-atom cluster and no basis functions on the outer four atoms. In this case, the central atom would be assigned the entire density matrix. However, in an infinite crystal, any appropriate basis would presumably have the full translational and rotational symmetry of the crystal's space group. In this limit, every equivalent unit of the crystal is assigned an equal portion of the density matrix. Thus, to the extent that the unit at the centre of the cluster is far from the boundaries, the Mulliken decomposition should give crystalline-type results for the central unit.

3. Spin multiplicity

The correct many-body wavefunction for the carbon cluster may be written as a sum

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over Slater determinants. In the UHF approximation, however, one selects the single Slater determinant that best represents the system under consideration. In particular, one must specify the spin[†], S, or equivalently, the multiplicity, $2S + 1$, of the Slater determinant. The spin determines the occupancy of the spin-up and spin-down orbitals. For the five-atom carbon cluster, $(15 + S)$ spin-up states and $(15 - S)$ spin-down states are occupied.

To obtain realistic surface states, one wants the spin state that gives the lowest energy for the cluster. Nothing guarantees, however, that the lowest energy state will give the best crystalline properties at the central atom. To study these equations, UHF calculations have been performed for cluster spins ranging from 0 to 6. Selected results are shown in table 1 and in figure 1.

Table 1. Dependence upon cluster spin (S) of the total cluster energy (TE), charge on the central atom (Q), valence band width (VBW), band gap (BG) and the difference between the (100) and (111) directional Compton profiles at $q = 0 (\Delta J(0))$. The row labeled 'atom' gives the total energy of five non-interacting carbon atoms with the same gaussian basis. The row labeled 'crystal' gives HF crystal results. The labels (LT) and (GT) indicate whether the cluster results are expected to be 'less than' or 'greater than' the crystalline or atomic results. All energies are in au.

S	TE			Q	VBW	BG	$\Delta J(0)$
atoms	(LT)		$-188\cdot4230$	6			
crystal	(GT)		$-189\cdot3348$	6	(LT) $1\cdot11$	(GT) $0\cdot52$	$0\cdot10$
0			$-188\cdot4172$	$6\cdot70$	$1\cdot15$	$0\cdot09$	$-0\cdot22$
1			$-188\cdot3169$	$6\cdot75$	$1\cdot20$	$0\cdot10$	$-0\cdot20$
2			$-188\cdot4668$	$6\cdot85$	$1\cdot16$	$0\cdot33$	$-0\cdot19$
3			$-188\cdot3789$	$6\cdot62$	$1\cdot14$	$0\cdot35$	$-0\cdot12$
4			$-188\cdot2701$	$6\cdot31$	$1\cdot03$	$0\cdot46$	$-0\cdot02$
5			$-188\cdot4153$	$6\cdot03$	$0\cdot91$	$0\cdot57$	$0\cdot10$
6			$-188\cdot6392$	$6\cdot17$	$0\cdot78$	$0\cdot67$	$0\cdot05$

The total cluster energy dips at spin 2, but is lowest for spin 6 (by 6 eV over the spin 0 energy). From the figure we see that only the clusters with spins 2 and 6 are bound with respect to the energy of the free atoms. The charge on the central atom will be six electrons in an infinite crystal. The central atom's charge for the cluster is closest to this value of six for spins 5 and 6. For the central atom, the difference between the directional Compton profiles in the (100) and (111) directions has the wrong sign at low spin, and is closest to the crystalline result for spins 5 and 6. Because the one-electron eigenvalues for the cluster form a subset of the crystalline eigenvalues, the valence band width (energy spread of the non-1s-like filled orbitals) of the cluster should be narrower than the crystalline HF bandwidth. Similarly, the bandgap (energy difference between the highest occupied and lowest empty orbitals) between empty and occupied states should be larger for the cluster than for the crystal. These inequalities also are met only at high spin.

We conclude for these reasons that the spin 6 state of the cluster gives the lowest total energy, the most realistic surface states, and the most crystalline results for the

[†] In UHF calculations, the wavefunction is not necessarily an eigenfunction of the spin. However, in the case of C_5, the expectation values of the spin were close to the integer values reported here.

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central atom. In this state, 21 electrons have spin up and 9 have spin down. Five electrons of each spin are in carbon 1s core states. Four of each spin are in bonding orbitals between the central atom and its nearest neighbours. The remaining 12 electrons all have spin
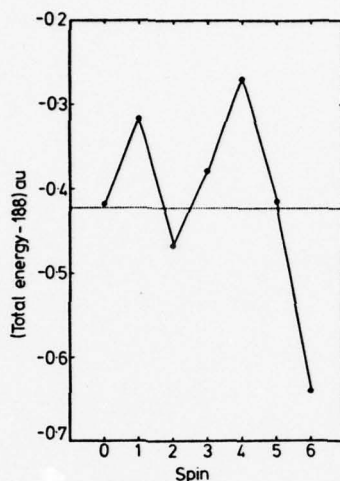

Figure 1. The total energy of the five-atom cluster carbon as a function of the spin, S, (more accurately, M_s). The broken line gives the energy of five isolated carbon atoms. The value for the infinite HF crystal would be $-189{\cdot}3348$ au.

up. They are therefore spatially orthogonal to each other and to the central bonding orbitals, so that they point roughly towards the (missing) 12 carbon atoms at the next-nearest-neighbour positions in diamond: $a/2(\pm 1, \pm 1, 0)$, $a/2(\pm 1, 0 \pm 1)$ and $a/2(0, \pm 1, \pm 1)$. They have gained 6 eV of exchange energy over the spin 0 state of the cluster.

This is an example of Hund's rule (Herzberg 1944), extended to molecules: 'Of the configurations given by equivalent electrons, those with the greatest multiplicity lie deepest ...'. If this rule were to hold for a more accurate representation of a surface on a covalently bound material, the electrons in the dangling bond surface states would all have the same spin.

4. X-ray structure factors

X-ray structure factors give a quantitative measure of the electronic charge distribution by providing the Fourier transform of the charge density for a given reciprocal lattice vector of the crystal.

$$S(k) = \int \exp(ik \cdot r)\, \rho(r, r)\, d(r). \tag{4}$$

In order to compare the structure factors for each atom of the cluster with those of the infinite crystal, we must first multiply the atom's structure factor obtained from the Mulliken-decomposed density matrix by $\exp(-k \cdot R_a)$ to remove a meaningless phase, and then impose the inversion symmetry of the diamond cubic crystal structure.

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$$\rho(r, r') = \rho(T - r, T - r') \tag{5a}$$

for

$$T = a/4 (1, 1, 1). \tag{5b}$$

We thereby form for an atom, a, of the cluster

$$\tilde{S}_a(k) = S_a(k) + \exp (ik \cdot T)S_a(-k). \tag{6}$$

The results are shown in table 2. With the exception of the (222) direction, the crystalline HF and the experimental structure factors are within 2% of each other, which is within both experimental and computational uncertainty. The tendency of the (222) results to be too small has been seen in other materials as well as diamond, and is probably due to a lack of d functions in the carbon basis. Results for the central atom of the cluster are considerably closer to the crystalline results than are the results for the surface atoms or for the average over all cluster atoms. Even for a cluster of as few as five atoms, the charge distribution associated with the central atom is already close to that of an atom in the perfect crystal.

Table 2 X-ray structure factors from experiment, from crystal HF, for the five individual carbon atoms at the given coordinates, for the average over the surface atoms, and for the average over the cluster. Diamond inversion symmetry is imposed as is described in the text.

	000	111	220	311	222
Experiment	6	3·32	1·98	1·66	0·14
Crystal HF	6	3·27	1·94	1·69	0·08
(0, 0, 0)	6·16	3·21	1·92	1·68	0·07
$a/4(1, 1, 1)$	5·96	3·22	1·99	1·85	0·01
$a/4(1, -1, -1)$	5·96	2·99	1·97	1·74	0·02
$a/4(-1, 1, -1)$	5·96	2·99	1·97	1·76	0·02
$a/4(-1, -1, 1)$	5·96	2·99	1·99	1·76	0·02
Surface	5·96	3·04	1·98	1·78	0·02
Cluster	6	3·08	1·97	1·76	0·03

5. Directional Compton profiles

Compton profiles are related to the electron momentum distribution, denoted $t(k)$. In the HF approximation,

$$t(k) = \sum_{\substack{\text{filled} \\ \text{states}}} |\phi(k)|^2 = \frac{1}{(2\pi)^3} \int \exp \left[ik \cdot (r - r') \right] \rho(r, r') \, d(r) \, d(r'). \tag{7}$$

In particular, in the impulse approximation, the Compton profile in the direction n is given by

$$J_n(q) = \int t(k)J(q - k \cdot n) \, d(k). \tag{8}$$

This is just an integral of the momentum distribution over a plane in k space at a distance, q, from the origin taken in the direction of n. The dependence of $J_n(q)$ on the direction, n, thus gives information about the bonding orbitals of diamond. Additionally, each Compton profile satisfies the sum rule

$$\int J_n(q) \quad dq = \int t(k) \, d(k) = \text{number of electrons}. \tag{9}$$

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It is well known that in materials like diamond, the crystal wavefunction has more high-momentum (high-k) components that it does in the atom, since the crystalline electrons are localized into a smaller volume. Therefore, because of the sum rule, the Compton profiles at zero momentum ($q = 0$) fall in going from the isolated atom to the crystal. This is illustrated in figure 2, where we see the progressive decrease in $J_{111}(q)$
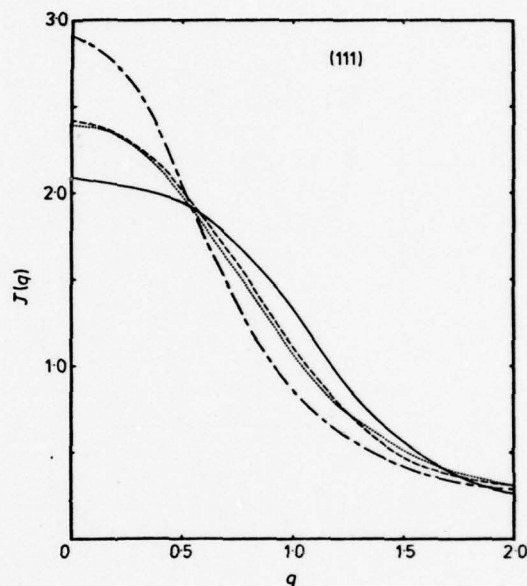

Figure 2. Compton profiles in the (111) direction for the carbon atom($-\cdot-\cdot-$), C_2 cluster ($----$), C_5 cluster ($-----$) and HF crystal ($———$).

from the atom to the C_2 molecule, to the C_5 cluster, and then to the infinite crystal. Because the cluster average for all five atoms is very close to the value for the central atom, we show the Compton profile for the average in the figure. It is obvious from the figure that a substantial amount of high-momentum character is still missing from the cluster Compton profile.

Figures 3(a)–(d) show the differences between the Compton profiles in various directions. These differences are in satisfactory agreement with experiment and with the crystal HF calculations for all of the cases except the (100) − (110). Significantly, the (110) direction in diamond corresponds to the direction of the next-nearest-neighbour of the central atom, and these atoms are not included in the cluster.

6. Summary and conclusions

We have seen that it is possible to obtain fairly reasonable crystalline x-ray structure factors and directional Compton profile differences for diamond from a cluster containing as few as five atoms. This cluster includes the dominant interactions in such a solid of the central atom with its nearest neighbours. It is essential, however, to choose that spin multiplicity for which all of the dangling orbitals have the same spin. One can then

eliminate the effects of these surface states from results to be attributed to the bulk by using the Mulliken population analysis which partitions the density matrix with respect to the individual atoms. From the results given above for five atoms. it is suggested that in the case of a cluster of 17 atoms (one carbon atom plus both its nearest and next-nearest neighbours) a spin state of 18 (36 dangling bonds at the surface) might give results for the central atom which would be in quite satisfactory agreement with crystalline
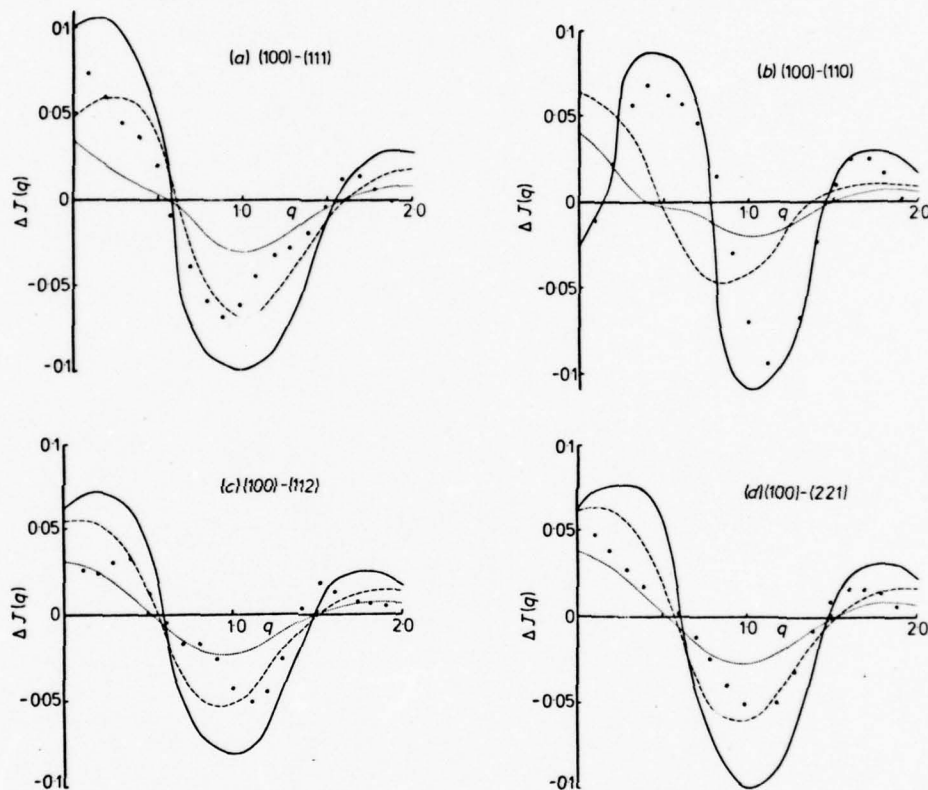
Figure 3. Directional Compton profile differences for experiment (· · ·). crystalline HF (————). cluster average (– – – –). and central atom of the cluster (— — — —). for (a) $(100) - (111)$, (b) $(100 - (110)$, (c) $(100) - (112)$, (d) $(100) - (221)$.

results. Further work is also in progress to investigate the relationship between the critical dependence of the cluster results and the spin multiplicity, and more realistic models of the diamond surface.

Acknowledgments

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APPENDIX B

THE ACCURACY OF FIRST-ORDER DENSITY MATRICES
OBTAINED BY ELECTRONIC STRUCTURE METHODS
INVOLVING THE VALENCE ELECTRONS ONLY

The accuracy of first-order density matrices obtained by electronic structure methods involving the valence electrons only

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First-order density matrices are obtained from all-electron unrestricted-Hartree–Fock (UHF) calculations and from effective-core-potential valence-electron UHF calculations for the silicon and argon atoms, and for the Si_2 molecule. The density matrices are compared by means of their derived X-ray scattering factors, directional Compton profiles, and the charge density, at selected points in **k** and **r** space.

I. INTRODUCTION

A central problem in molecular and solid-state computational physics involves the calculation from first principles of the electronic first-order density matrix.[1,2] Quantities derivable from the density matrix, such as X-ray scattering factors and directional Compton profiles are measurable to high precision—often to within one percent.[3]

For molecular systems with constituent atoms heavier than neon, it rapidly becomes very expensive to perform electronic structure calculations involving all of the electrons. Procedures based upon pseudopotential theory have recently been developed for reducing the all-electron (AE) molecular problem to a valence-electron (VE) problem.[4] The tightly bound core electrons ($1s^2 2s^2 2p^6$ for silicon and argon, for example) are assumed to have the same wavefunctions as in the isolated atoms. An effective core potential (ECP) is constructed directly from the atomic Hartree–Fock equations, following a well defined pseudo-orbital transformation, to represent the effect of the frozen core orbitals on the remaining electrons. The VE problem in the field of the effective core potentials is then solved by the standard electronic structure methods.

The purpose of this paper is to compare first-order density matrices calculated from AE UHF calculations with those obtained from ECP-VE UHF calculations to obtain an estimate of the percent deviation, and hence of the percent reliability of the ECP density matrix. Comparisons will be made of three quantities derived from the density matrix: X-ray scattering factors, directional Compton profiles, and the electronic charge density.

We have chosen three systems for comparison: the open-shell silicon atom, the closed shell argon atom, and the diatomic molecule Si_2.

II. CALCULATION OF THE ONE-ELECTRON DENSITY MATRIX

The one-electron density matrix is obtained from the electronic wavefunction by the relation[5]

$$\rho(\mathbf{r}, \mathbf{r}') = N \int [\Psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)$$

$$\times \Psi^*(\mathbf{r}', \mathbf{r}_2, \ldots, \mathbf{r}_N) d(\mathbf{r}_2) \ldots d(\mathbf{r}_N)/\langle \Psi \Psi \rangle], \quad (1)$$

and the expectation value of any one-electron operator is given by

$$\langle \hat{P} \rangle = \int \delta(\mathbf{r}' - \mathbf{r}) \hat{P}(\mathbf{r}') \rho(\mathbf{r}, \mathbf{r}') d(\mathbf{r}) d(\mathbf{r}') . \quad (2)$$

The all-electron wavefunction is

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$
$$= A[\varphi_{1a}\alpha \cdots \varphi_{na}\alpha\varphi_{1b}\beta \cdots \varphi_{nb}\beta\Theta_v(1, \ldots, N-2n)], \quad (3)$$

where $\{\varphi_{ia}\varphi_{ib}, \; i = 1, \ldots, n\}$ are the core orbitals, and Θ_v is the valence wavefunction. In the UHF approximation, the valence wavefunction is given by

$$\Theta_v = \varphi_{(n+1)a}\alpha \cdots \varphi_{(n+na)a}\alpha\varphi_{(n+1)b}\beta \cdots \varphi_{(n+nb)b}\beta \quad (4)$$
$$(2n + na + nb = N) .$$

If the valence and core orbitals form an orthogonal set, then the first-order density matrix is given by the well-known expression

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{k=1}^{n+na} \varphi_{ka}(\mathbf{r})\varphi_{ka}^*(\mathbf{r}') + \sum_{k=1}^{n+nb} \varphi_{kb}(\mathbf{r})\varphi_{kb}^*(\mathbf{r}') . \quad (5)$$

However, one of the essential changes introduced in the reduction of the AE problem to a VE problem is the lifting of the core orthogonality requirement on the valence orbitals.[4] The orthogonality effects are folded into the effective core potentials. The modified valence orbitals are smooth nodeless orbitals[4] which are not orthogonal to the core orbitals. It is therefore incorrect to use Eq. (5) for the density matrix, when the valence orbitals are determined from a VE calculation.

In order to obtain the correct expression for the one-electron density matrix, it is convenient to transform from the nonorthogonal sets of core and valence orbitals, $\{\varphi_{ka}, \; k = 1, \ldots, n+na\}$ and $\{\varphi_{kb}, \; k = 1, \ldots, n+nb\}$ to sets of orthonormal orbitals, $\{\psi_{ka}, \; k = 1, \ldots, n+na\}$ and $\{\psi_{kb}, \; k = 1, \ldots, n+nb\}$. The orthonormalizing transformation may generally be written as

$$\psi_{ka} = \sum_{i=1}^{n+na} \varphi_{ia}A_{ik} \qquad k = 1, n+na , \quad (6a)$$

$$\psi_{kb} = \sum_{i=1}^{n+nb} \varphi_{ib}B_{ik} \qquad k = 1, n+nb , \quad (6b)$$

where the A and B matrices satisfy the conditions

$$A^\dagger \Delta_A A = 1 , \quad (7a)$$

$$B^\dagger \Delta_B B = 1 , \quad (7b)$$

and where

$$(\Delta_A)_{ij} = \langle \varphi_{ia} | \varphi_{ja} \rangle \quad ,$$

and

$$(\Delta_B)_{ij} = \langle \varphi_{ib} | \varphi_{jb} \rangle \quad .$$

We note that the UHF wavefunction constructed from the nonorthogonal orbitals is, apart from a constant, equal to a UHF wavefunction constructed from the orthogonal orbitals. Therefore, the correct expression for the one-electron density matrix is

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{k=1}^{n+na} \psi_{ka}(\mathbf{r})\psi_{ka}^*(\mathbf{r}') + \sum_{k=1}^{n+nb} \psi_{kb}(\mathbf{r})\psi_{kb}^*(\mathbf{r}') \quad . \tag{8}$$

Inserting Eq. (6) in Eq. (8), we obtain

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{n+na} \sum_{j=1}^{n+na} \varphi_{ia}(\mathbf{r})(AA^+)_{ij}\varphi_{ja}^*(\mathbf{r}')$$
$$+ \sum_{i=1}^{n+nb} \sum_{j=1}^{n+nb} \varphi_{ib}(\mathbf{r})(BB^+)_{ij}\varphi_{jb}^*(\mathbf{r}') \quad . \tag{9}$$

The general form of the A and B transformation matrices satisfying Eqs. (7) is[6]

$$A = \Delta_A^{-1/2} U_A \quad , \tag{10a}$$

$$B = \Delta_B^{-1/2} U_B \quad , \tag{10b}$$

where U_A and U_B are arbitrary unitary matrices. It follows readily that

$$AA^+ = \Delta_A^{-1} \tag{11a}$$

and

$$BB^+ = \Delta_B^{-1} \quad . \tag{11b}$$

Therefore, the correct expression for the UHF one-electron density matrix is

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{n+na} \sum_{j=1}^{n+na} \varphi_{ia}(\mathbf{r})(\Delta_A^{-1})_{ij}\varphi_{ja}^*(\mathbf{r}')$$
$$+ \sum_{i=1}^{n+nb} \sum_{j=1}^{n+nb} \varphi_{ib}(\mathbf{r})(\Delta_B^{-1})_{ij}\varphi_{jb}^*(\mathbf{r}') \quad . \tag{12}$$

To obtain the above, we have used some special properties of the UHF wavefunction. For multideterminantal wavefunctions, Ψ, the transformations of the type (6) will, in general, transform Ψ into a manifold of determinants of types possibly not present previously. However, once Ψ is reexpressed in terms of the orthonormal set of orbitals, it is straightforward to obtain the one-electron density matrix by use of Eq. (1).

The procedure outlined above for constructing the density matrix from nonorthogonal core and valence orbitals [Eq. (12)] can be contrasted with a method outlined earlier, Eq. (9) of Ref. 7, in which the valence orbitals were explicitly orthogonalized to the core orbitals. However, in Ref. 7, the resulting core-orthogonalized valence orbitals were never made mutually orthogonal to each other.

III. ONE-ELECTRON PROPERTIES CALCULATED FROM THE DENSITY MATRIX

The one-electron properties considered here are (i) the charge density $\sigma(\mathbf{r}) = \int \delta(\mathbf{r}' - \mathbf{r})\rho(\mathbf{r}, \mathbf{r})d(\mathbf{r}') = \rho(\mathbf{r}, \mathbf{r})$, which is simply the diagonal part of the density matrix,

TABLE I. All-electron (AE) and ECP valence electron eigenvalues for argon and silicon atoms and for the molecule Si_2. The double entries for atomic silicon give the spin-up and spin-down UHF Eigenvalues. [a]

		AE		ECP-VE	
Argon	$3s$	-1.275		-1.274	
	$3p$	-0.589		-0.589	
Silicon	$3s$	-0.618	-0.461	-0.619	-0.458
	$3p_{x,y}$	-0.297		-0.297	
Si_2	$4\sigma_g$	-0.690		-0.683	
	$4\sigma_u$	-0.489		-0.493	
	$2\pi_{ux,uy}$	-0.281		-0.277	

[a]All quantities are expressed in atomic units. See Ref. 9.

(ii) the X-ray scattering factor $S(\mathbf{k}) = \int \sigma(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}d(\mathbf{r})$, which is the Fourier transform of the charge density, and (iii) the directional Compton profile (in the impulse approximation)

$$J_n(q) = \int t(\mathbf{k})\delta(\mathbf{n}\cdot\mathbf{k} - q)d(\mathbf{k}) \quad ,$$

which is obtained by integrating the electron momentum distribution, $t(\mathbf{k})$, over a plane normal to a vector n at a distance q from the origin in momentum space. The momentum distribution, $t(\mathbf{k})$, is obtained by separate Fourier transforms in $\mathbf{r}$ and $\mathbf{r}'$ of $\rho(\mathbf{r}, \mathbf{r}')$,

$$t(\mathbf{k}) = \frac{1}{(2\pi)^6} \int \int e^{i\mathbf{k}\cdot\mathbf{r}}\rho(\mathbf{r}, \mathbf{r}')e^{-i\mathbf{k}\cdot\mathbf{r}'}d(\mathbf{r})d(\mathbf{r}') \quad .$$

IV. CALCULATIONAL DETAILS

The first system chosen for detailed study is the open shell silicon atom in the ^3P state. The valence spin-orbital product is

$$(3s_a\alpha)(3s_b\beta)(3p_{xa}\alpha)(3p_{ya}\alpha) \quad .$$

The basis consists of Huzinaga's $(14s10p)$ Cartesian Gaussian basis contracted to a $[4s3p]$ set.[8] The total energy for this basis is -288.8465 hartrees.[9]

The closed shell argon atom was chosen as the second system. We use Huzinaga's $(14s10p)$ Gaussian basis for argon,[8] contracted to a $[4s3p]$ set. The total energy is then -526.79957 hartrees.

The same silicon Gaussian basis was used for the UHF calculation on the $^1\Sigma_g^+$ state of Si_2. The interatomic separation used is 4.4352 bohr.[9] The total energy is then -577.6263 hartrees. The valence configuration is

$$(4\sigma_g^2)(4\sigma_u^2)(2\pi_{yu}^2)(2\pi_{xu}^2) \quad .$$

In all cases, the same basis was used for the AE calculation and for the ECP-VE calculation, although in practice a much smaller basis suffices for the ECP-VE calculation because of the smoothness of the valence pseudo-orbitals.[4] Table I shows a comparison of the orbital energies from the AE and ECP-VE calculations. This comparison shows agreement of the eigenvalues to within 0.007 hartrees.

The parameters specifying the effective core potentials for both silicon and argon were taken from the recent work by Topiol.[10]

TABLE II. Calculated X-ray structure factors, $S(K)$, and directional compton profiles, $J_n(q)$, for atomic silicon.[a,b]

	k or q	AE	Eq. (12)(%)[c]	Eq. (5) (%)[d]
S_{100}	0.2	13.77	0.00	0.06
	0.4	13.14	0.01	0.22
	1	10.55	0.03	0.84
	2	8.11	0.13	0.29
	4	5.29	0.38	−1.74
S_{001}	0.2	13.84	0.00	0.04
	0.4	13.38	0.01	0.16
	1	11.20	0.03	0.69
	2	8.42	0.13	0.59
	4	5.28	0.39	−1.38
J_{100}	0	4.74	−0.09	2.19
	0.4	3.86	−0.10	2.41
	1	1.73	−0.18	1.05
	2	1.04	−0.12	−3.53
	4	0.37	0.62	−1.97
J_{001}	0	5.83	−0.06	1.80
	0.4	3.70	−0.09	3.05
	1	1.58	−0.23	0.11
	2	1.05	−0.14	−4.00
	4	0.37	0.63	−1.25

[a]The ^3P silicon wavefunction has the ^3p_x and ^3p_y one-electron orbitals occupied. Thus the S_{100} and J_{100} refer to K and n within the plane of symmetry.
[b]All quantities are expressed in atomic units. See Ref. 9.
[c]The column headed "Eq. 12" gives the percent deviation of ECP results from the all-electron results (AE), when Eq. (12) is used to calculate the total (core plus valence) density matrix.
[d]The column headed "Eq. (5)" is similarly defined.

V. RESULTS

The all-electron results and the precent deviations in the ECP valence electron results, by use of both the approximate density matrix expression, Eq. (5), and the

TABLE III. Calculated x-ray structure factors and directional compton profiles for atomic argon.[a]

		AE	Eq. (12) (%)	Eq. (5) (%)
$S(K)$	0.2	17.83	0.00	0.05
	0.4	17.34	0.00	0.19
	1	14.63	0.00	1.02
	2	10.19	0.00	2.13
	4	6.86	0.00	−1.69
$J(q)$	0	5.04	0.00	1.77
	0.4	4.62	0.00	2.01
	1	2.66	0.00	3.90
	2	1.09	0.00	0.58
	4	0.52	0.00	−7.08
$\sigma(r)$	0	2826.	0.02	−0.78
	0.08	246.6	−0.03	−1.40
	0.4	8.61	−1.20	−5.38
	0.6	1.81	−1.60	2.67
	1.	0.447	0.04	−1.37
	1.5	0.186	0.12	−7.27
	2	0.0601	0.10	−7.8
	4	0.00057	0.06	−7.36

[a]See the caption to Table II for details.

TABLE IV. Calculated x-ray structure factors, $S(K)$, directional Compton profiles, $J_n(q)$, (both per atom), and the charge density $\sigma(r)$ are given for Si_2.[a]

		AE	Eq. (12) (%)	Eq. (5) (%)
$S(K)_{100}$	0.2	12.52	0.01	0.05
	0.4	8.54	0.03	0.17
	1	−6.51	0.09	0.78
	2	−2.28	0.25	0.78
	4	−4.49	0.38	−1.35
$S(K)_{001}$	0.2	13.76	0.00	0.06
	0.4	13.11	0.01	0.21
	1	10.51	0.03	0.80
	2	8.13	0.11	0.27
	4	5.29	0.37	−1.63
J_{100}/at	0	6.42	0.09	2.16
	0.4	3.61	−0.33	3.04
	1	1.52	−0.15	−0.84
	2	1.04	−0.10	−3.80
	4	0.368	0.65	−1.20
J_{001}/at	0	4.79	−0.14	2.07
	0.4	3.89	−0.10	2.35
	1	1.71	−0.16	0.90
	2	1.04	−0.09	−3.40
	4	0.37	0.59	−1.80
$\sigma(r)$	0	0.0314	−0.24	−6.8
	0.4435	0.0366	0.01	−5.2
	1.109	0.129	−0.91	3.09
	1.44	0.812	−1.42	0.11
	1.88	8.39	0.95	−2.37
	2.22	1288	0.01	−0.44
	2.62	6.42	0.12	−2.35
	3.22	0.218	−1.22	2.46
	4.22	0.0213	0.01	−6.76

[a]The column headings are defined in the caption of Table II. The line joining the silicon atoms is in the (100) direction.

more correct expression, Eq. (12), are shown in Tables II, III, and IV. In all cases, the ECP-VE x-ray scattering factors and Compton profiles derived from Eq. (12) are within 0.7% of the AE results, while the use of the approximate density expression, Eq. (5), leads to results which are off by as much as 7% for argon atom and 3% for the silicon atom and Si_2 molecule. The charge densities are also off by 7% for the approximate density expression, Eq. (5) and by less than 1% for the more correct expression, Eq. (12).

VI. CONCLUSIONS

Quantities derivable from the first-order density matrix can be reliably obtained from effective-core-potential valence-electron calculations to within roughly one percent of the all-electron results if the nonorthogonality of the core and pseudovalence orbitals is correctly taken into account (Eq. 12). If the nonorthogonality is ignored and use is made of the standard expression, Eq. (5), errors as large as 7% are introduced. If the coreorthogonalized valence orbitals are not mutually orthogonalized, errors of several percent are introduced.[7]

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APPENDIX C

UHF CALCULATIONS FOR 15-ATOM LITHIUM CLUSTERS

APPENDIX C

UHF CALCULATIONS FOR 15-ATOM LITHIUM CLUSTERS

A series of symmetry-restricted, spin-unrestricted (UHF) Hartree-Fock calculations were carried out on a 15-atom lithium cluster in a body-centered cubic structure with a lattice constant of 3.48 angstrom (6.57638 bohr). Most of the calculations were carried out with a minimal STO-3G basis set,[1] but a limited study was also conducted with a double-zeta basis (obtained by removing the outermost primitive Gaussian function from the 2s and 2p contractions in the STO-3G basis) on the innermost nine atoms, while retaining the fully-contracted STO-3G basis for the outer six atoms. As is seen from Table I, this procedure is quite risky, as it tends to concentrate the charge in the region for which a richer basis set is provided, and should not be used with basis sets as small as those employed here (except perhaps for larger clusters, where the peripheral atoms may have a weaker effect on the results at the center of the cluster).

A multiplicity study, in which UHF results were obtained for resultant spin S between 1/2 and 15/2 (multiplicity 2S+1 between 2 and 16) is described in Tables C1 to C4. The lowest energy is obtained for S=3/2 (quartet), unlike the situation in diamond-structure carbon clusters, which tend to have all peripheral dangling-bond electrons with the same spin. This appears to reflect the metallic structure of lithium, compared to the covalent structure in diamond. However, as in the case of the five-atom carbon cluster (Appendices A and D), the lowest energy is obtained when there are no partially-occupied sets of degenerate (t or e symmetry) orbitals. These are the cases in which the spin-up and spin-down electrons, separately, form closed-shell-

like structures, while the higher energy cases generally involve some t or

e orbitals which are partially filled in either the spin-up or the spin-down

states, or in both.   On the other hand, the most even charge distributions

are obtained for S=5/2 to 9/2.

More useful results, which could be directly comparable to experi-

ment, would require a larger basis set (a full double-zeta basis on each atom),

and thus more computer time than was available in the present study.

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TABLE CI

Effect of basis set in UHF calculations
on 15-atom lithium cluster.[a]

	Basis 1	Basis 2
Total energy (hartrees)	-110.03720	-110.12425
Fermi Level (hartrees)		
Spin up	-0.1138	-0.1309
Spin down	-0.1040	-0.1092
Charge per atom (electrons)		
Shell 0	2.8124	3.0466
Shell 1	3.0030	3.2215
Shell 2	3.0273	2.6969

(a) Spin state $S=4$. Basis 1 is [2s1p] (STO-3G) on all 15 atoms.
     Basis 2 is [3s2p] on the nine atoms in shells 0 and 1, and
     [2s1p] on the six atoms in shell 2.

FIGURE CAPTIONS

Fig. C1   Total energy as a function of spin state S for fifteen-atom lithium cluster, using the STO-3G basis.

Fig. C2   Highest occupied orbital energy (Fermi level) as a function of spin state S for fifteen-atom lithium cluster, using the STO-3G basis.

Fig. C3   Energy per atom (Mulliken projection) as a function of spin state S for fifteen-atom lithium cluster, using STO-3G basis.

Fig. C4   Electronic charge per atom (Mulliken gross atomic population) as a function of spin state S for fifteen atom lithium cluster, using STO-3G basis.
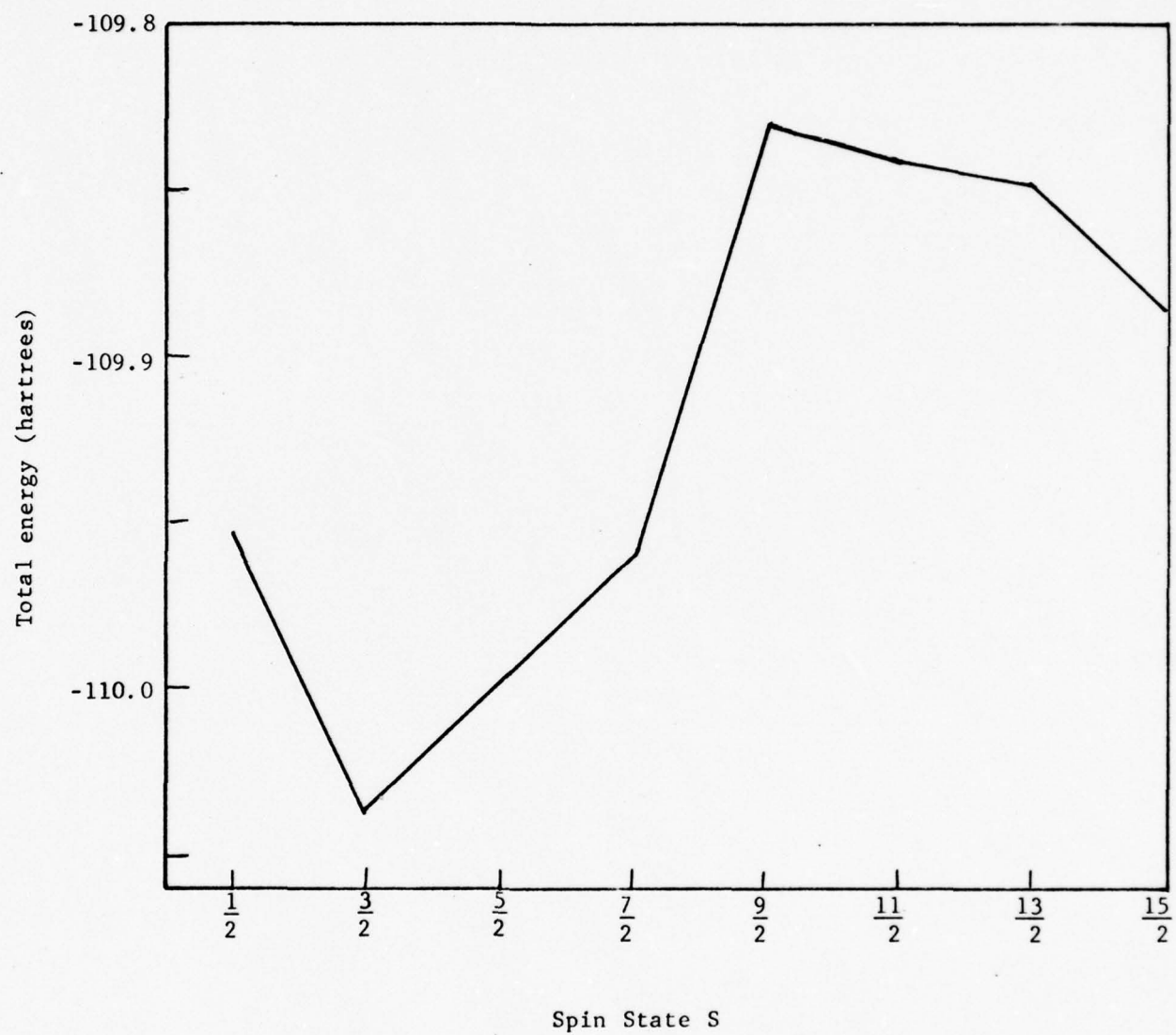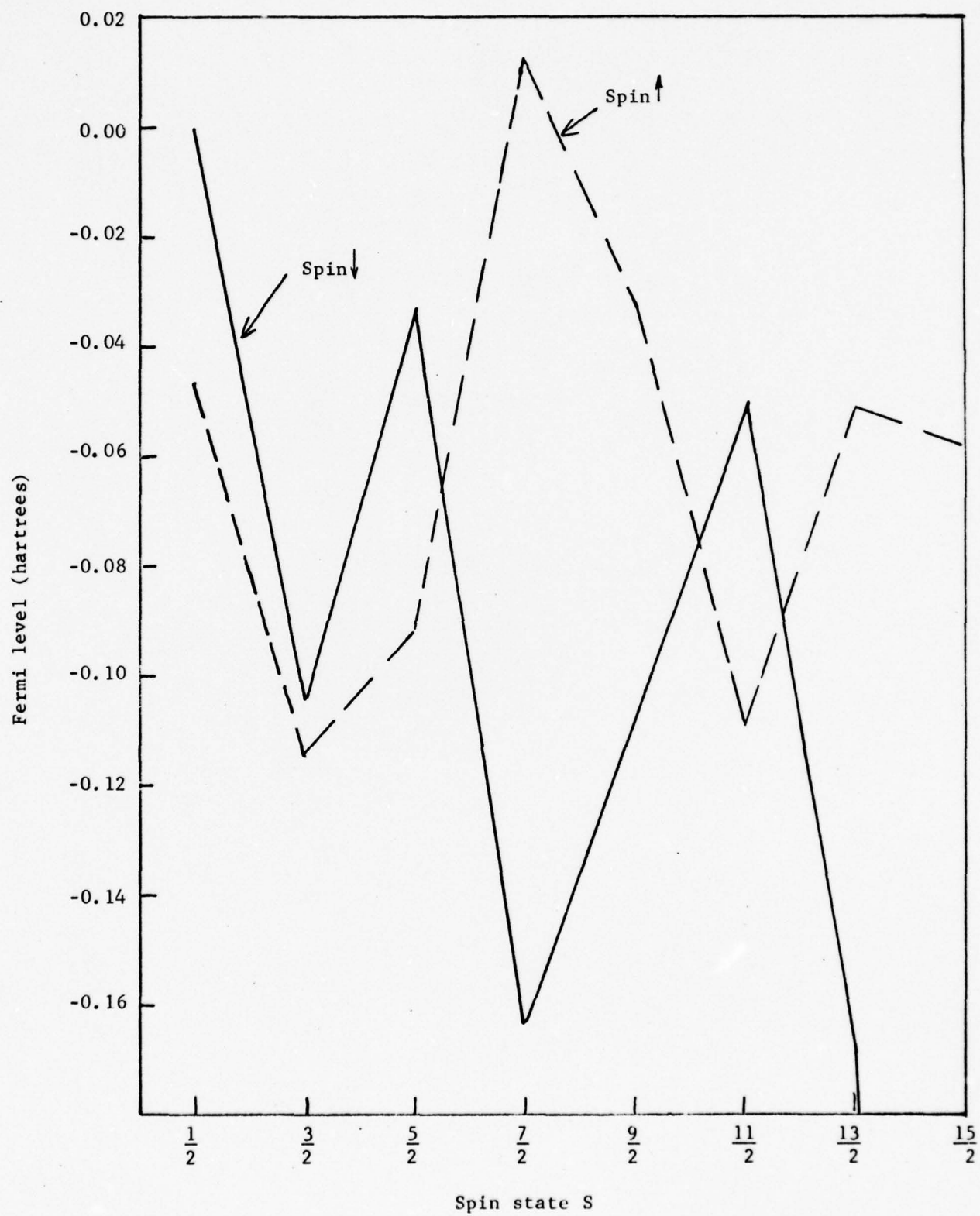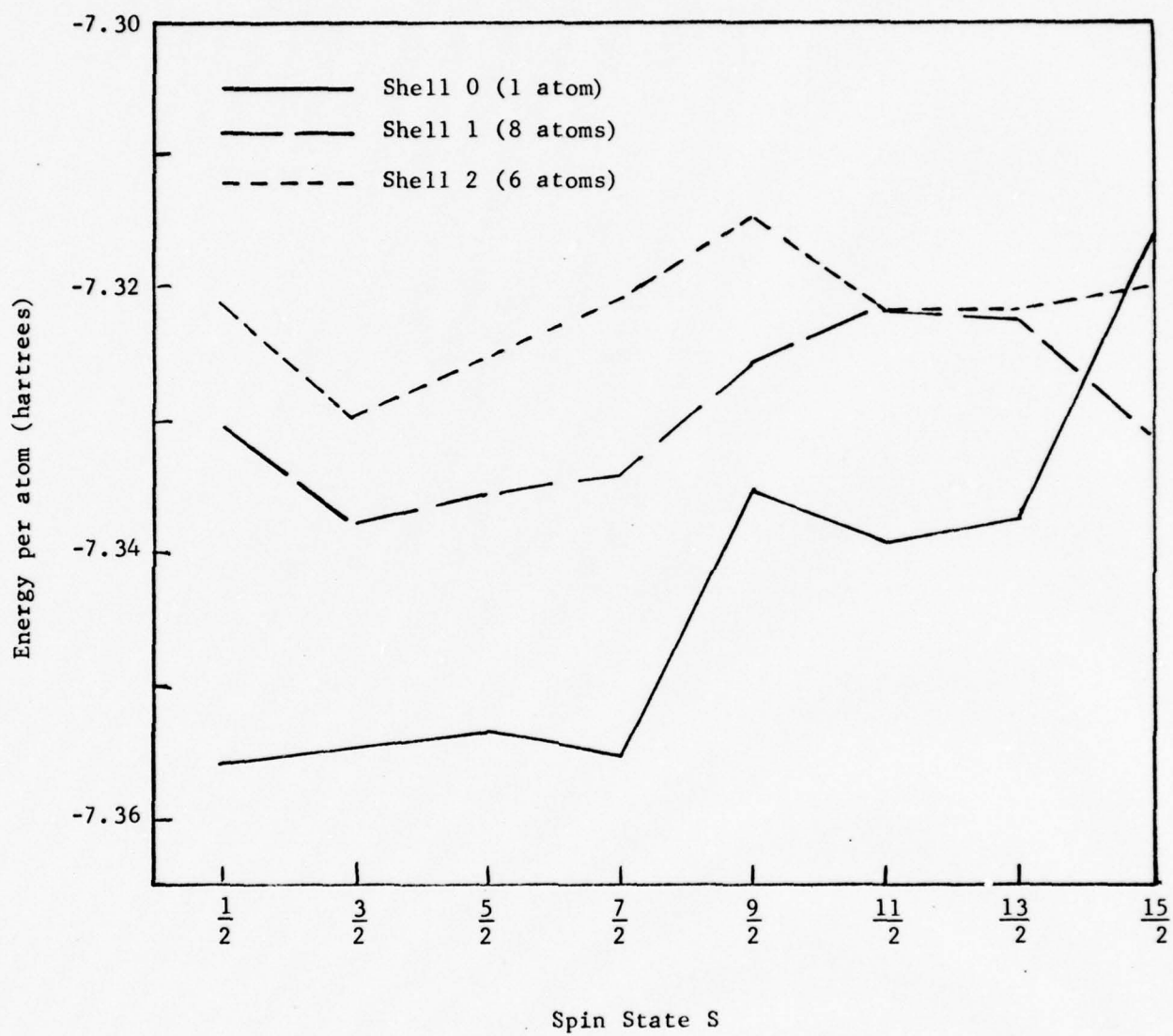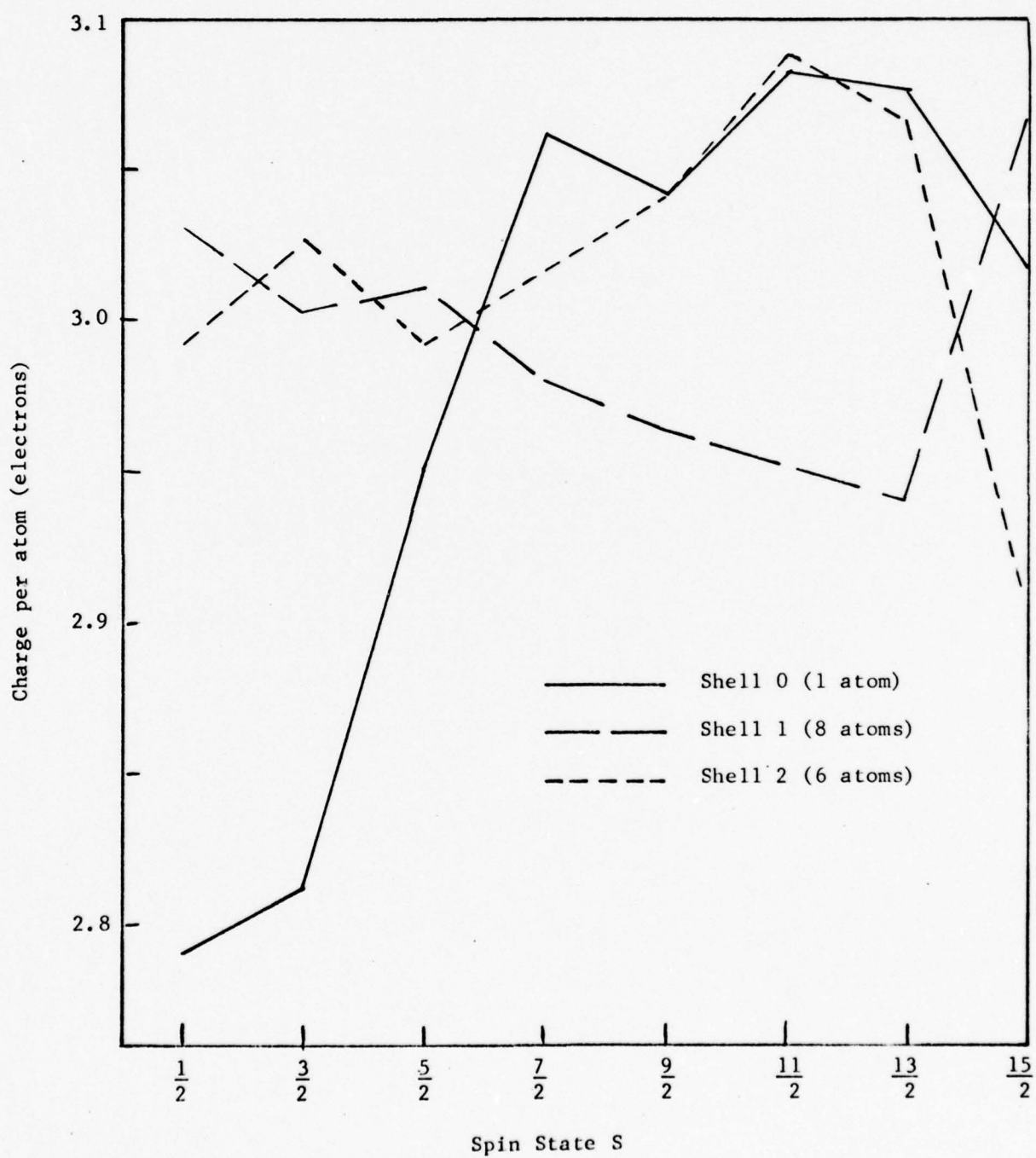
Fig. C1

Fig. C2

Fig. C3

Fig. C4

APPENDIX D

USE OF PSEUDOPOTENTIALS IN CARBON
ATOM CLUSTER CALCULATIONS

APPENDIX D

USE OF PSEUDOPOTENTIALS IN CARBON ATOM CLUSTER CALCULATIONS

Four series of symmetry-restricted, spin-unrestricted Hartree-Fock (UHF) calculations were carried out for the five-atom carbon cluster:

(1) All-electron calculations with a standard double-zeta Huzinaga-Dunning basis set.[1] These will be referred to as AE(SB) (all electron, standard basis).

(2) All-pseudopotential calculations, in which the two core electrons on each atom were replaced by a Kahn-Baybutt-Truhlar pseudopotential,[2] using the same standard basis set as in (1). These will be referred to as AP(SB) (all pseudo, standard basis).

(3) Pseudo-shell calculations, in which the core electrons on the peripheral four atoms were replaced by pseudopotentials, while all six electrons on the central atom were treated explicitly. The standard basis was used. These will be referred to as PS(SB) (pseudo shell, standard basis).

(4) Same as (3), but the special valence-only basis of Kahn, Baybutt, and Truhlar[2] was used for the peripheral four atoms. These will be referred to as PS(VB) (pseudo shell, valence basis).

A comparison of series (1) and (2) allows a general assessment of the effect of the use of pseudopotentials on molecular computational results. A comparison of series (2) and (3) allows an examination of the idea of treating peripheral atoms in a cluster by a lower-order approximation than was used for the central atom (or atoms). This examination is facilitated by examining properties projected for the central atom in the cluster.[3,4] A comparison of series (3) and (4) provides an assessment of the effect of the use of a valence-only basis for those atoms which are treated in a pseudopotential approximation.

The use of such a basis is essential if the full economies of the pseudo-potential approach are to be realized in calculations on larger clusters.

For each series, calculations were carried out for total spin S ranging from zero to six or seven (multiplicity one to thirteen or fifteen), and as in previous calculations,[3] it was found that the results for S=6, with twelve parallel spins representing the twelve dangling bonds on the peripheral four atoms, produced the lowest cluster energy and most closely represented the situation in the diamond cluster.

The principal results of these calculations are shown in Tables DI to DV and Figures D1 to D4. A more complete account is being prepared for publication.

It is clear from the results given that the calculations which utilize the core approximation reproduce the trends and characteristics of the all-electron calculations. Central-atom (projected) results for the pseudo-shell (PS) calculations are particularly close to the all-electron results, while total cluster results for all the pseudopotential calculations are quite close to each other, and often could not be resolved from each other on the scale of the plots. For the variation of energy with lattice constant, the pseudo-shell results are seen to reproduce the all-electron results much better than the all-pseudo treatments.

The use of a valence basis on those atoms for which the core approximation is invoked is seen to have little effect on the results except in the case of the vacant orbital energies. As is well known from molecular calculations, the vacant orbitals are particularly sensitive to the choice of basis, and have little individual significance except in minimal basis calculations.

Thus it is seen that the use of a core approximation together with a valence
basis is a viable approach for the treatment of peripheral atoms in cluster
calculations.   In treatments of clusters of heavier atoms, successively more
electron shells can be treated by this approximation as one proceeds from the
center of the cluster to its periphery, resulting in significant economies in
computational effort.

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    T. H. Dunning, Jr., J. Chem. Phys. 53, 2823 (1970).

2. L. R. Kahn, P. Baybutt, and D. G. Truhlar, J. Chem. Phys. 65, 3826 (1976).

3. S. Goldstein, L. A. Curtiss, and R. N. Euwema, J. Phys. C 9, 4131 (1976), included as Appendix A.

4. R. N. Euwema and L. R. Kahn, J. Chem. Phys. 66, 306 (1977), included as Appendix B.

TABLE DI.

Energies of five-atom carbon cluster as a function of spin state S, for different types of calculation, in hartrees.[a]

S	Total Energy				Central Atom Energy AE(SB)
	AE(SB)	AP(SB)	PS(SB)	PS(VB)	
0	−188.4019	−188.4632	−188.4549	−188.4580	−37.9080
1	.3030	.3643	.3562	.3602	.9042
2	.4520	.5142	.5059	.5114	.9144
3	.3690	.4293	.4209	.4289	.8927
4	.2452	.3245	.3157	.3285	.8363
5	.4076	.4758	.4664	.4844	.8852
6	.6380	.7122	.7055	.7183	.9291
7	−187.8963	−187.9959	−187.9733	−	.6102

[a] The notation for the different types of calculation is described in the text. The energies for the pseudopotential calculations include core contributions computed from the difference in the energies of single-atom calculations with and without the core approximation (with the corresponding bases). The lattice constant is 3.56 angstrom.

TABLE DII.

Ionization potentials of five-atom cluster as a function of spin state S, for different types of calculation, in electron volts.[a]

S	AE(SB)	AP(SB)	PS(SB)	PS(VB)
0	7.96 ↑	8.11 ↑	8.08 ↑	8.18 ↓
1	4.65 ↑	4.05 ↓	4.04 ↓	4.14 ↓
2	7.31 ↑	7.45 ↑	7.45 ↑	7.57 ↑
3	9.07 ↓	9.16 ↓	9.16 ↓	9.10 ↓
4	5.35 ↑	5.05 ↓	5.05 ↓	4.98 ↓
5	7.50 ↓	7.47 ↓	7.36 ↓	7.25 ↓
6	11.01 ↑	11.10 ↑	11.07 ↑	11.11 ↑
7	−0.02 ↑	0.56 ↑	0.02 ↑	−

[a]The ionization potentials are the Koopmans theorem values (i.e., the negatives of the highest occupied orbital energy). The arrows next to the entries indicate whether the highest occupied orbital has spin up or spin down.

TABLE DIII.

Compton profiles (per atom) of five-atom cluster
in (1,0,0) direction for S=6, for different types
of calculation.[a]

q	AE(SB)	AP(SB)	PS(SB)	PS(VB)
For total cluster				
0.0	2.464	2.508	2.498	2.458
0.5	1.985	1.975	1.976	1.989
1.0	1.049	1.029	1.034	0.981
1.5	0.504	0.496	0.498	0.500
2.0	0.303	0.302	0.303	0.304
For atom 1				
0.0	2.354	2.446	2.382	2.517
0.5	1.964	1.972	1.977	2.097
1.0	1.049	1.026	1.050	1.071
1.5	0.486	0.474	0.484	0.486
2.0	0.289	0.287	0.288	0.288
For atoms 2-5				
0.0	2.492	2.524	2.526	2.444
0.5	1.990	1.975	1.976	1.962
1.0	1.050	1.030	1.030	1.030
1.5	0.508	0.501	0.501	0.504
2.0	0.306	0.306	0.306	0.307

[a]Atom 1 is the central atom, in the (0,0,0)
position. The core contribution to the pseudo-
potential results was taken from a comparison of
single-atom calculations with and without the
core approximation.

TABLE DIV

Compton profiles (per atom) of five-atom cluster in (1,1,1) direction for S=6, for different types of calculation.[a]

q	AE(SB)	AP(SB)	PS(SB)	PS(VB)
		For total cluster		
0.0	2.431	2.476	2.465	2.427
0.5	1.976	1.968	1.969	1.979
1.0	1.080	1.062	1.066	1.070
1.5	0.508	0.514	0.499	0.503
2.0	0.295	0.293	0.294	0.295
		For atom 1		
0.0	2.315	2.405	2.341	2.480
0.5	1.927	1.941	1.944	2.062
1.0	1.120	1.100	1.124	1.144
1.5	0.496	0.474	0.489	0.492
2.0	0.271	0.264	0.267	0.267
		For atom 2		
0.0	2.573	2.601	2.602	2.558
0.5	1.942	1.937	1.934	1.906
1.0	1.128	1.113	1.112	1.102
1.5	0.491	0.472	0.477	0.482
2.0	0.269	0.263	0.265	0.268
		For atoms 3-5		
0.0	2.423	2.457	2.460	2.366
0.5	2.004	1.987	1.989	1.976
1.0	1.051	1.032	1.031	1.034
1.5	0.517	0.511	0.510	0.513
2.0	0.312	0.312	0.312	0.313

[a] Atom 1 is the central atom and atom 2 is in the (1,1,1) position. The core contribution to the pseudopotential result was taken from a comparison of single atom calculations with and without the core approximation.

TABLE DV.

Compton profile of the central atom in five atom cluster at q=0 as a function of spin state S, for different types of calculation.[a]

S	AE(SB)	AP(SB)	PS(SB)	PS(VB)
		(1,0,0) direction		
0	2.117	2.188	2.115	2.145
1	2.181	2.258	2.184	2.182
2	2.281	2.357	2.286	2.269
3	2.302	2.382	2.309	2.295
4	2.187	2.288	2.215	2.213
5	2.124	2.209	2.137	2.190
6	2.354	2.446	2.382	2.517
7	1.883	2.075	1.960	–
		(1,1,1) direction		
0	2.341	2.424	2.354	2.401
1	2.386	2.470	2.399	2.411
2	2.470	2.554	2.484	2.479
3	2.428	2.507	2.435	2.436
4	2.223	2.307	2.236	2.253
5	2.041	2.120	2.050	2.119
6	2.315	2.405	2.341	2.480
7	2.436	2.570	2.504	–

[a] The core contribution to the AP(SB) result was obtained from a comparison of single-atom calculations with and without the core approximation.

FIGURE CAPTIONS

Fig. D1   Total energy of five-atom cluster as function of spin state
S, for different types of calculation. The notation is
described in the text. The results for PS(VB) are indistin-
guishable from those for PS(SB) on the scale of this graph.
See also Table I.

Fig. D2   Orbital energies of five-atom cluster for S=6, for different
types of calculations. The numbers next to the orbital levels
specify the degeneracy of each orbital.

Fig. D3   Valence band width and band gap of five-atom cluster as a
function of spin state S, for different types of calculation.
The results for PS(SB) and PS(VB) are indistinguishable from
those for SP(SB) on the scale of this figure. The points
marked with an asterisk are those for which there is overlap
between an occupied spin-up band and a vacant spin-down band,
or vice versa. This happens when a set of degenerate orbitals
is partially filled, and results from the imposition of spatial
symmetry on the orbitals.

Fig. D4   Cluster energy of five-atom cluster as a function of lattice
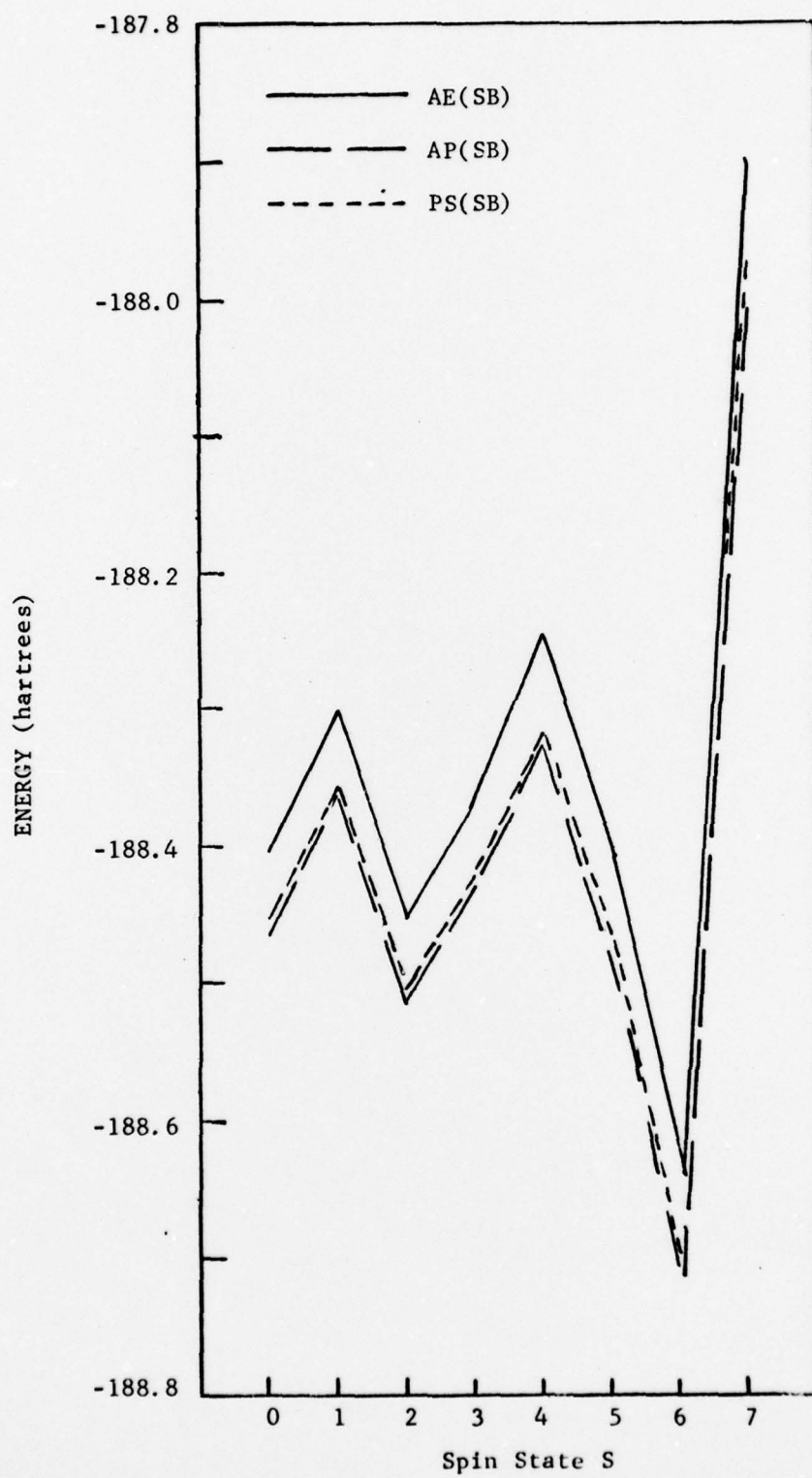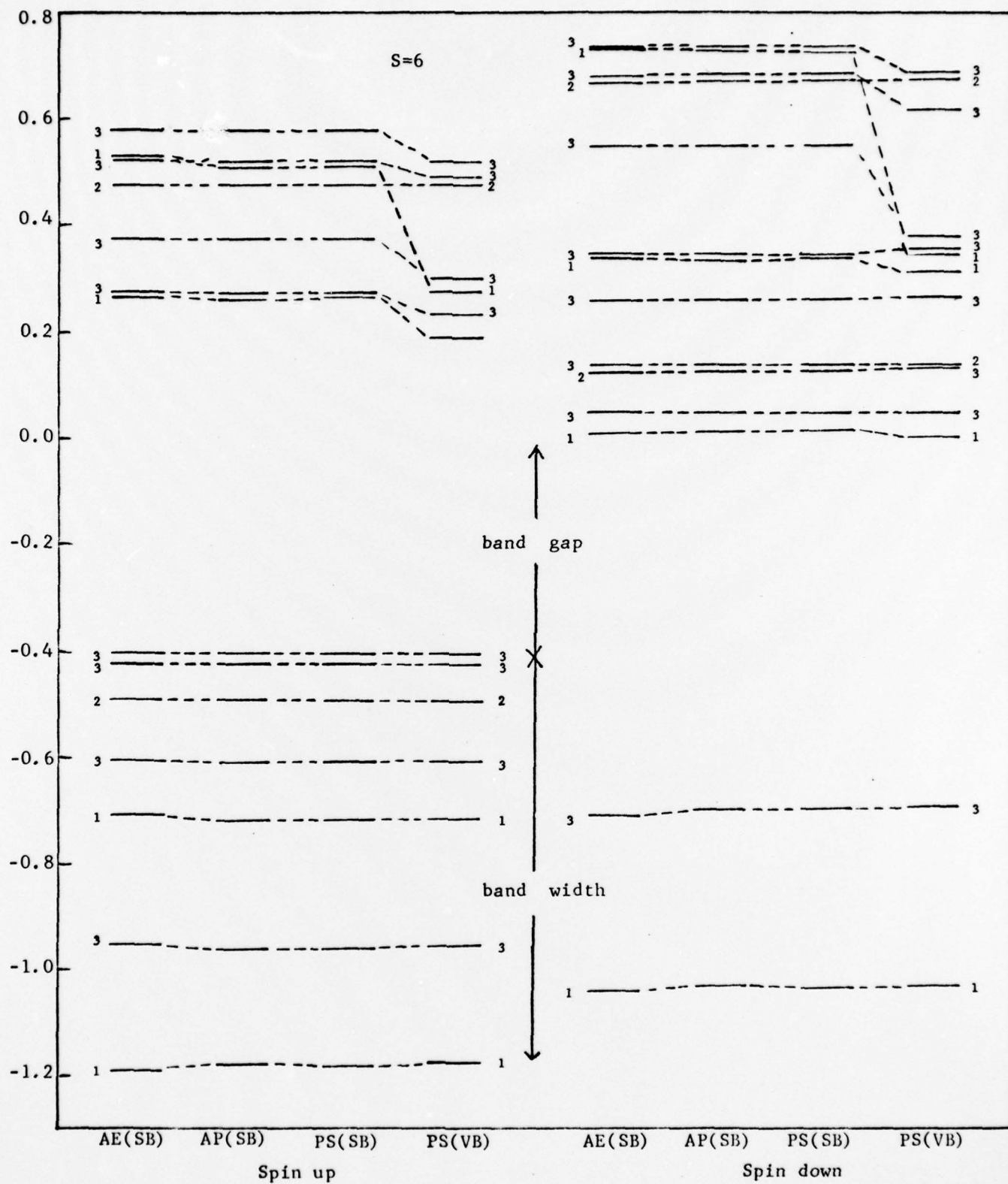constant, for S=6, for different types of calculation.

Fig. D1

Fig. D2
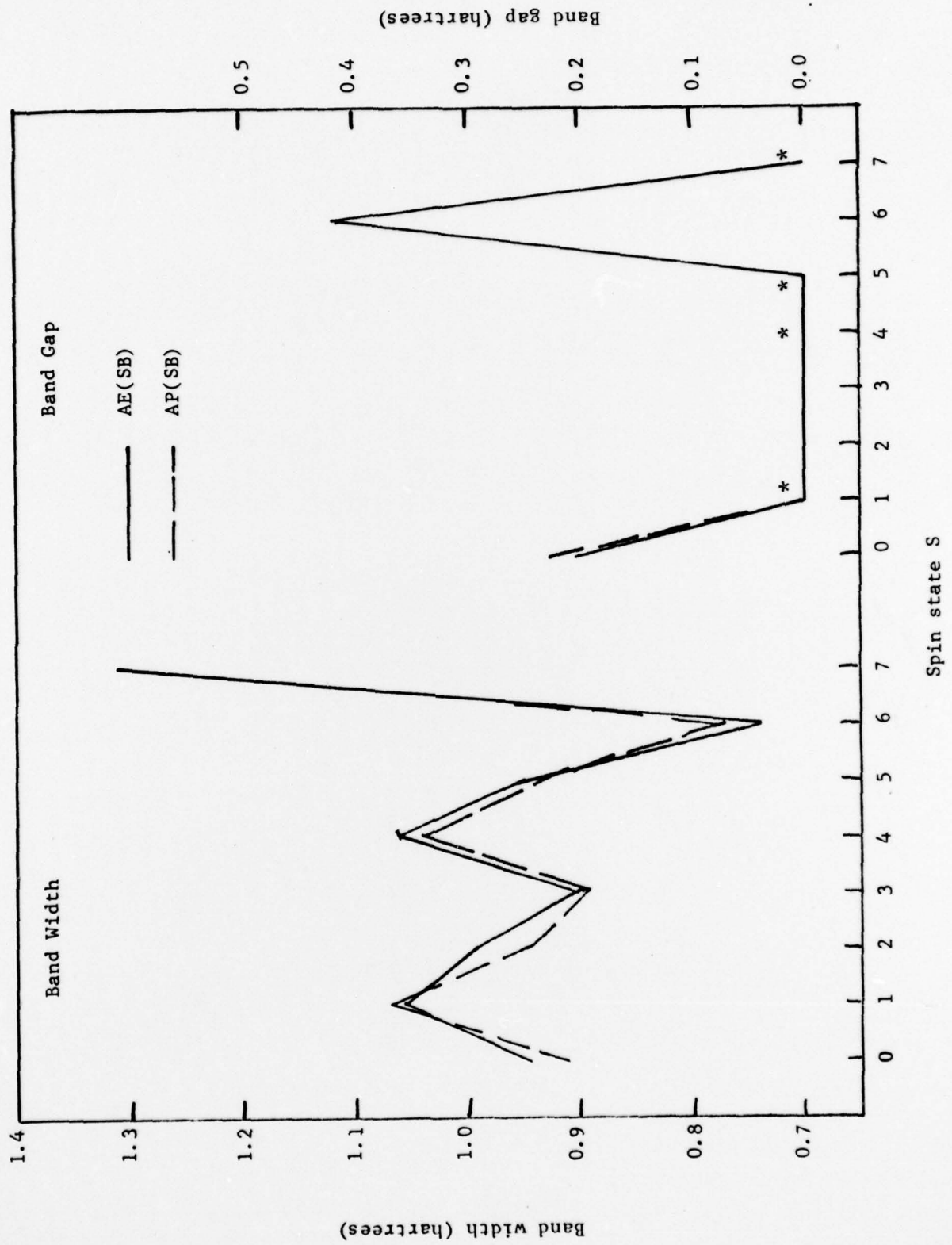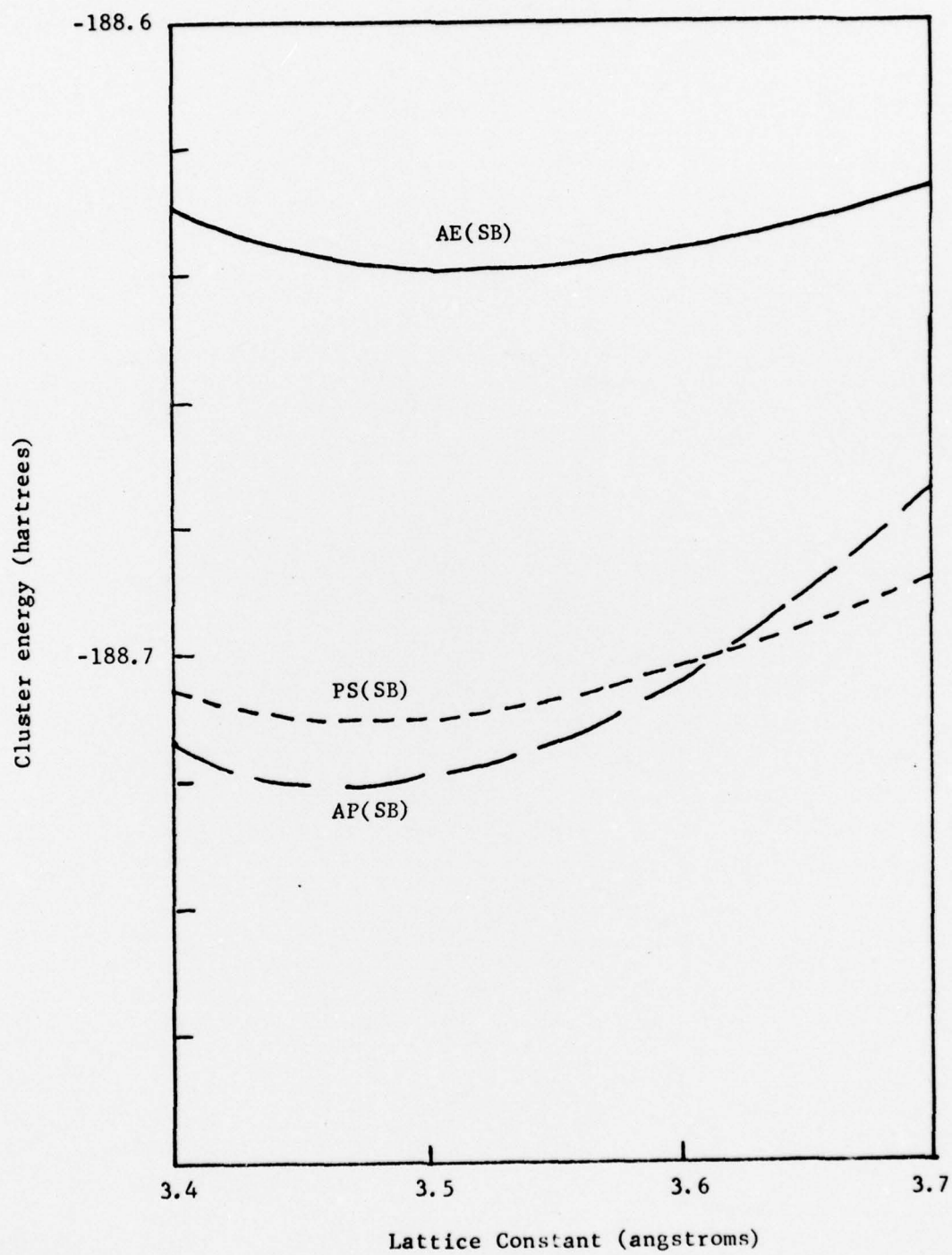
Fig. D3

Fig. D4

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